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Abstract

The occupied and unoccupied density of states (ODOS and UDOS) predicted by cluster calculations of PuO_2 and UO_2 are directly compared to the results from soft X-ray spectroscopy.

Direct Comparison of Spectroscopic Data with Cluster Calculations of Plutonium Dioxide and Uranium Dioxide*

I. Introduction

Using spectroscopic data produced in the experimental investigations of bulk systems, including X-Ray Absorption Spectroscopy (XAS), Photoelectron Spectroscopy (PES) and Bremstrahlung Isochromat Spectroscopy (BIS) [1-5], the theoretical results within for UO_2 and PuO_2 clusters [6] have been evaluated. The calculations of the electronic structure of the clusters have been performed within the framework of the Relativistic Discrete-Variational Method (RDV). [6,7] The comparisons between the LLNL experimental data and the Russian calculations are quite favorable. The cluster calculations may represent a new and useful avenue to address unresolved questions within the field of actinide electron structure.

II. Experimental

The experiments were performed in house at Lawrence Livermore National Laboratory and offsite using synchrotron radiation from the Advanced Light Source at Lawrence Berkeley National Laboratory in Berkeley, CA. For the UO_2 XAS measurements, a depleted UO_2(100) single crystal of ~3 X 3 mm^2 with thickness of ~0.5 mm was prepared from a large crystal. Sample dimensions were chosen to minimize the activity while being consistent with the x-ray beam spot. The UO_2 XAS measurements were performed at Beam Line 8. [8] Further detail for the UO_2 XAS can be found in References 2 and 5. The Resonant Photoemission of the Pu samples was carried out on Beam Line 7. [9] The Pu spectroscopy experiments were performed upon three bulk Pu samples, each having a mass of approximately 30 mg. Two of the samples were new and highly purified; the third was an aged, less purified sample. The new Pu samples were taken from a specially purified batch of Pu metal. The

product of the purification process was alpha-Pu containing a total of 170-ppm wt impurities. A more complete description of the sample preparation and experimental measurements can be found in Reference 3. The XPS and BIS of UO_2 measurements were carried out at LLNL. [1, 10, 11] The experiments were performed in a combined BIS/Fano spectrometer. [12] The UO_2 was formed in the following manner: by polishing a polycrystalline uranium sample and exposing it to air at ambient pressure and room temperature. The polycrystalline uranium sample was of very high purity stock that had been used extensively in earlier experiments. Details of those earlier experiments and the nature of the high purity U can be found elsewhere. [Reference 10 and references therein.] The extensive Ultraviolet (UPS) and X-ray (XPS) measurements confirmed the quality of the UO_2 sample. [10]

III. Discussion and Summary

In the cluster calculations, the central part of the cluster is that which is most bulk-like. The comparisons between experiment and theory with thus be made using the central part of the cluster.

The uranium dioxide case is shown in Figure 1. Here, an approximation for the occupied density of states is gotten from the X-ray photoelectron spectroscopy (XPS) results and the unoccupied density of states (UDOS) from the X-ray Absorption Spectroscopy (XAS) and Bremstrahlung Isochromat Spectroscopy (BIS) data. Of course, all of the data of each of these spectroscopies include cross-sectional effects. Thus, the experimental DOS estimates are skewed by the specific cross sections. The lower half of the figure includes partial and total density of states calculations for the 7p, 7s, 6d and 5f states of Uranium and the 2p states of Oxygen, from the central part of a

$U_{63}O_{216}$ cluster. On the Occupied Density of States (ODOS) side, the experimental U5f and O2p peaks match quite closely with their theoretical ODOS counterparts. On the Unoccupied Density of States (UDOS) side, both the XAS and BIS features match up with the appropriate theoretical O2p, U5f, and U6d counterparts. The only manipulation of the experimental spectra was to align the centroid of the leading edge of each spectrum with the energy zero in the calculations. Thus, the centroid of the leading edge is treated as if it were a Fermi Edge. This alignment of the leading edges at the energy zero is tantamount to assuming a zero direct band-gap, the justification of which is discussed in Reference 6.

Next, the plutonium dioxide case will be considered: the data is plotted in Figure 2. Because only photoelectron spectroscopy data was available for this comparison, only the occupied density of states will be discussed. The theoretical Occupied Density of States (ODOS) is shown for the $6p_{1/2}$, $6p_{3/2}$, 5f, 6d, 7s and 7p of Pu and the 2p and 2s of Oxygen, for the central part of the $Pu_{63}O_{216}$ cluster. The experimental synchrotron radiation photoelectron spectrum is from a slightly oxidized Pu sample, taken at the Cooper Minimum using a photon energy of 225 eV. By working at the Cooper Minimum, the non-Pu5f features are emphasized. Again, the only manipulation is to align the Fermi Edge of the PES spectrum with the energy zero of the calculations. The result is again very good agreement, including the placement of the $Pu6p_{1/2}$, O2s, $Pu6p_{3/2}$, O2p and Pu5f peaks.

Thus it can be seen that the cluster calculations achieve a very accurate approximation of bulk electronic structure in their central parts, for the systems of uranium dioxide and plutonium dioxide.

Acknowledgements

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Figure Captions

Figure 1 A comparison of the Density of States (DOS) for the central part of a $U_{63}O_{216}$ cluster with spectroscopic results from a bulk UO_2 sample. The Occupied Density of States (ODOS) is compared to the data from X-ray Photoelectron Spectroscopy (XPS). The Unoccupied Density of States (UDOS) is compared to the X-ray Absorption Spectroscopy (XAS) and Bremstrahlung Isochromat Spectroscopy (BIS) data. Partial and total DOS are provided. The spectroscopic data are representative of experimental DOS estimates, although skewed by cross-sectional effects.

Figure 2 A comparison of the Density of States (DOS) for the central part of a $Pu_{63}O_{216}$ cluster [6] with spectroscopic results from a slightly oxidized bulk Pu sample. [3,4] The Occupied Density of States (ODOS) is compared to the data from synchrotron-radiation-based Photoelectron Spectroscopy (PES). Partial and total DOS are provided. The spectroscopic data are representative of experimental DOS estimates, although skewed by cross-sectional effects. By working at the Cooper Minimum, the non-5f features are emphasized. Please see the text for detail.

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Figures

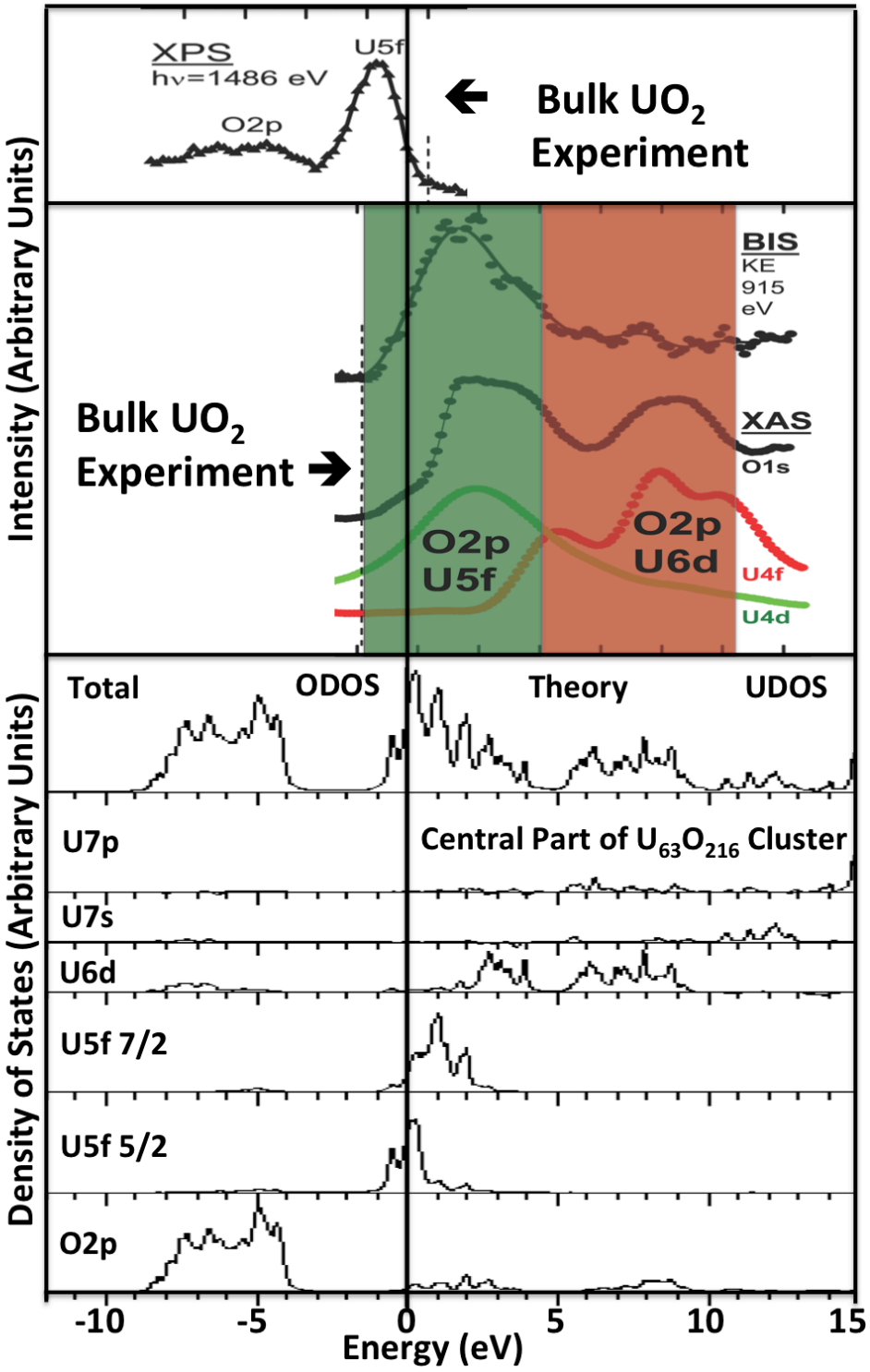

Figure 1

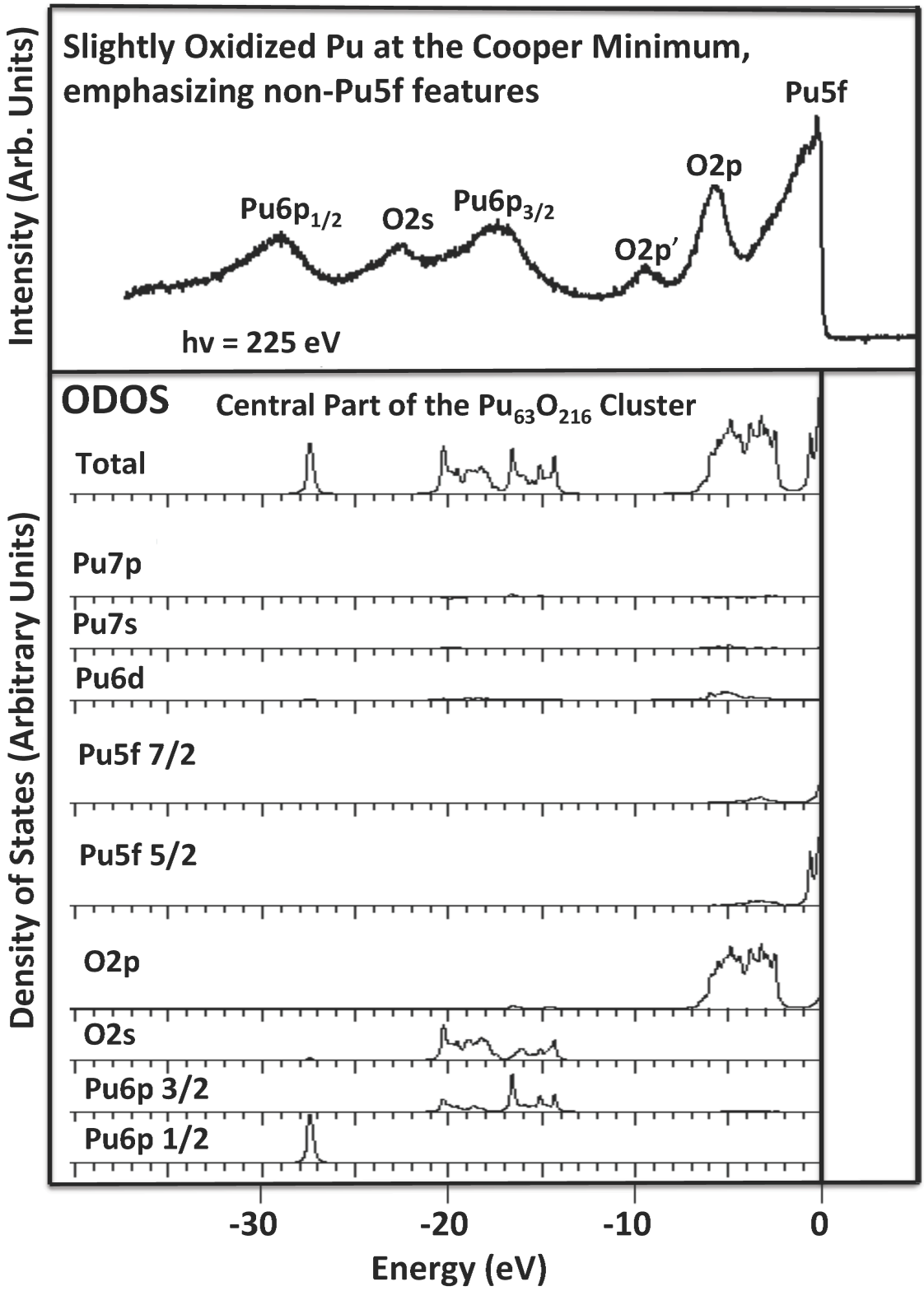
Slightly Oxidized Pu at the Cooper Minimum,
emphasizing non-Pu5f features
Pu5f
O2p
Pu6p1/2
O2s
Pu6p3/2
O2p'
hv = 225 eV
Intensity (Arb. Units)
ODOS
Central Part of the Pu63O216 Cluster
Total
Pu7p
Pu7s
Pu6d
Pu5f 7/2
Pu5f 5/2
O2p
O2s
Pu6p 3/2
Pu6p 1/2
Density of States (Arbitrary Units)
-30
-20
-10
0
Energy (eV)

Figure 2